

(19) World Intellectual Property Organization  
International Bureau



PCT



(43) International Publication Date  
18 May 2007 (18.05.2007)

(10) International Publication Number  
**WO 2007/055498 A1**

(51) International Patent Classification:  
C23C 22/00 (2006.01)

Gangoe-myeon, Chungwon-gun, Chungcheongbuk-do  
363-954 (KR).

(21) International Application Number:  
PCT/KR2006/004588

(74) Agent: SON, Min; 19th Floor, City Air Tower 159-9, Sam-seong-dong, Gangnam-gu, Seoul 135-973 (KR).

(22) International Filing Date:  
6 November 2006 (06.11.2006)

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data:  
10-2005-0108255  
11 November 2005 (11.11.2005) KR

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (for all designated States except US): KOREA INSTITUTE OF INDUSTRIAL TECHNOLOGY [KR/KR]; 35-3, Hongchon-Ri, Ipchang-Myun, Chonan-si, Chungcheongnam-do, Seoul 330-825 (KR).

(72) Inventors; and

(75) Inventors/Applicants (for US only): LEE, Young Chul [KR/KR]; 13-1004, Samho Apt., Bangbaebon-dong, Seocho-gu, Seoul 137-759 (KR). KIM, Myeong Jun [KR/KR]; 301-1108, Jugong 11-danji, Backseok-dong, Chonan-si, Chungcheongnam-do 330-788 (KR). YANG, Yun Shik [KR/KR]; 213-501, Samsung Raemian 2-cha Apt., Jangan 2-dong, Dongdaemoon-gu, Seoul 130-762 (KR). PARK, Mee-Young [KR/KR]; 60-38, Osong-2-gu,

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ORGANO CLAY CONTAINING ANTICORROSIVE COATING COMPOSITION AND PREPARATION METHOD THEREOF

(57) Abstract: Disclosed are an anticorrosive composition and a preparation method thereof, in which a general anticorrosive coating composition, composed of a monomer or a polymer having a reactive group, dissolved in an organic solvent, and a curing agent, as main components and an additive, further includes organoclay that is dispersed in the main components using ultrasonic waves. The method of preparing the composition includes uniformly dispersing organoclay in a monomer or a polymer having a reactive group, dissolved in an organic solvent, and/or a curing agent having an amine group, using ultrasonic waves, mixing the monomer or polymer having a reactive group with the curing agent, in which the organoclay is uniformly dispersed, and then adding an additive thereto. The anticorrosive composition can be used in various coatings including a zinc steel plate for automobiles, therefore remarkably increasing corrosion resistance.

WO 2007/055498 A1

## ORGANO CLAY CONTAINING ANTICORROSIVE COATING COMPOSITION AND PREPARATION METHOD THEREOF

### Technical Field

5           The present invention relates to an organoclay-containing anticorrosive coating composition and a preparation method thereof. More particularly, the present invention relates to an anticorrosive composition, comprising a curable monomer or polymer, such as epoxy,  
10       which is dissolved in an organic solvent, a curing agent, having two or more amine groups, and organoclay, which is uniformly mixed and dispersed in either or both of the monomer or polymer and the curing agent or in the mixture of the two components using ultrasonic waves, and to a  
15       method of preparing the same. The coating composition according to the present invention is a coating agent having corrosion resistance for preventing the corrosion of the surface of metal, such as a zinc plated steel plate, but the present invention is not limited thereto.

20

### Background Art

          Generally, the surface of a cold rolled steel plate is plated with metal, such as zinc, to impart the steel plate with corrosion resistance, therefore resulting in  
25       zinc plated steel plates and other plated steel plates. When such a metal plated steel plate is exposed to moisture

or air for a long time period, metal oxide, such as white rust and/or red rust, is formed.

Further, corrosion resistance treatment of a zinc-nickel plated steel plate for use in automobiles is chiefly realized by applying chromate and then coating with organic resin. However, according to the recent trend away from the use of chromium, which is harmful to human bodies, the function of the resin coating layer becomes more important (Park, Chan Seop et al., Polymer Science & Technology, 12(5), 660, 2001).

Accordingly, with the goal of increasing corrosion resistance without the use of chromium, a chromium-free anticorrosive coating agent and a preparation method thereof are disclosed in Korean Patent Nos. 443259 and 428562. Specifically, Patent No. 443259 discloses a coating composition prepared by adding alumina sol, serving as a main component, with predetermined amounts of alkylsilane, a specific aqueous polymer, and a molybdenum-containing corrosion inhibitor, and Patent No. 428562 discloses a coating composition, composed of 80~50 wt% of a resin mixture comprising aqueous organic resin and an inorganic component mixed at a solid content ratio of 70:30~30:70, 10~40 wt% of a phosphate-based rust inhibitor of metal oxide, and 1~20 wt% of an organo-metallic complex.

In addition, Korean Examined Patent Publication No. 2005-63979 discloses a resin composition for a pre-sealed

steel plate, comprising 100 parts by weight of epoxy resin, having a number average molecular weight of 15,000~60,000, 5~30 parts by weight of polymer-clay nanocomposite, 5~20 parts by weight of melamine resin, 1~5 parts by weight of wax, and 80~300 parts by weight of metal powder.

In the Examined Patent Publication No. 2005-63979, in the case where such a coating composition composed of the polymer-clay nanocomposite is applied on a zinc plated steel plate, the properties of the resin coating are evaluated while the molecular weight and the amount of the epoxy resin, the amount of the curing agent, and the amount of the polymer-clay nanocomposite are varied. Additionally, in the case where a predetermined composition ratio is provided, as in the claims of the above patent publication, a coating composition having good corrosion resistance and electrodeposition applicability is reportedly obtained.

The present invention, carried out by the present inventors aiming to avoid the problems encountered in the related art, resulted in the finding that a coating composition, prepared by uniformly dispersing organoclay in epoxy resin having a molecular weight different from that disclosed in the Examined Patent Publication No. 2005-63979 and/or a melamine curing agent using a predetermined process and then mixing them with other coating components, can have superior corrosion resistance. That is, in the above examined patent publication, the case where the epoxy

resin, having the molecular weight disclosed above, is not used is disclosed to make it impossible to assure good effects. However, in the case where an epoxy monomer or oligomer having a molecular weight much lower than that disclosed in the above examined patent publication is used and organoclay is uniformly dispersed using the process of the present invention before the epoxy resin and the curing agent, that is, the main components, are mixed, or in a state in which only the main components are mixed to thus prepare a coating composition, the coating composition thus prepared can exhibit corrosion resistance superior to that disclosed in the above examined patent publication.

## **Disclosure**

### **15 Technical Problem**

Accordingly, an object of the present invention is to provide a novel anticorrosive coating composition, comprising an epoxy monomer or oligomer and a melamine curing agent, in which organoclay is uniformly dispersed through a new process using ultrasonic waves.

Another object of the present invention is to provide a method of preparing an anticorrosive coating composition having improved corrosion resistance, comprising uniformly dispersing organoclay in an epoxy monomer or oligomer and/or a melamine curing agent using ultrasonic waves and then mixing them with an additive.

A further object of the present invention is to provide an anticorrosive coating composition, which does not include chromium (Cr), which is harmful to human bodies, and is thus environmentally friendly for application on the surface of any kind of metal, for example a zinc plated steel plate.

Yet another object of the present invention is to provide a coating composition, which can be applied on various surfaces to thereby increase corrosion resistance.

10

#### **Best Mode**

According to a first preferred aspect of the present invention, the invention provides an anticorrosive coating composition, comprising 100 parts by weight of an epoxy resin monomer or oligomer, 5~80 parts by weight of a curing agent having two or more amine functional groups, and 0.1~20 parts by weight of organic clay, which is uniformly mixed and dispersed in either or both of the epoxy monomer or oligomer and the curing agent.

According to a second preferred aspect of the present invention, the invention provides an anticorrosive coating composition, comprising 100 parts by weight of an epoxy monomer or oligomer having a number average molecular weight of 340~2,000 g/mole, 5~80 parts by weight of a curing agent having two or more amine functional groups, and 0.1~20 parts by weight of organoclay, uniformly mixed

and dispersed in either or both of the epoxy monomer or oligomer and the curing agent.

In the preferred aspects of the present invention, the organoclay, which is uniformly mixed and dispersed in  
5 either or both of the epoxy monomer or oligomer and the curing agent, is characterized in that uniform mixing and dispersion thereof can be realized using ultrasonic waves. Further, the mixing and dispersion of the organoclay may be conducted in respective components before mixing the above  
10 two components, or alternatively, the above two components are mixed and then the organoclay is mixed and dispersed therein.

Thus, according to a third preferred aspect of the present invention, the invention provides a method of  
15 preparing the uniformly dispersed organoclay-containing anticorrosive coating composition according to the first and second aspects, comprising

(i) uniformly dispersing 0.1~20 parts by weight of organoclay in either or both of 100 parts by weight of an  
20 epoxy resin monomer or oligomer and 5~30 parts by weight of a curing agent having two or more amine functional groups using ultrasonic waves, and then mixing the epoxy resin monomer or oligomer with the curing agent, either or both of which have the organoclay dispersed therein, or

25 (ii) mixing 100 parts by weight of an epoxy resin monomer or oligomer with 5~30 parts by weight of a curing

agent having two or more amine functional groups, and then uniformly dispersing 0.1~20 parts by weight of organoclay in the mixture using ultrasonic waves.

Preferably, as well as the main components, such as the epoxy resin, the curing agent, and the organoclay, the anticorrosive composition of the present invention may further comprise additive components, including an inorganic material, such as alumina or silica sol, which does not participate in the curing reaction in the coating composition, metal powders for increasing weldability, wax for increasing lubricating properties, a phosphate-based rust inhibitor, and an organo-metallic complex. In addition, other coating additive components, which are well known to those skilled in the art, may be further included. Optionally, any component may be variously selected from among the above-mentioned additive components, depending on the end use of the coating composition, which will be apparent to those skilled in that art. In the method of preparing the anticorrosive coating composition of the present invention, after mixing the main components of the coating composition according to the procedure of (i) or (ii), the additive component may be added thereto and thus mixed.

In the composition, the curing agent having two or more amine functional groups includes primary amines, secondary amines, tertiary amines, quaternary amines, and



all amine derivatives, and is preferably exemplified by a melamine curing agent.

The epoxy monomer, having epoxy groups attached to both ends thereof, reacts with an amine group to thus  
5 produce a polymer. The epoxy monomer useful in the present invention includes a modified epoxy monomer having a functional group, such as a halogen group or an amine group. Examples of the melamine derivative having two or more amine groups for use in polymerization or curing of  
10 the epoxy include methoxymethyl melamine, methoxymethyl butoxymethyl melamine, and hexamethoxymethyl melamine.

The nanocomposite of polymer and clay has good mechanical properties such as tensile strength, heat resistance, and permeation barrier effects to gases, such  
15 as oxygen, and moisture, and therefore is under thorough study at present. The clay generally indicates inorganic chemical material composed of silicate having a layered structure, in which the layers are in the form of an irregular disk with a thickness of about 1 nm and a  
20 diameter of about 0.1~100  $\mu\text{m}$ .

Examples of the clay include kaolin, serpentine, mica, vermiculite, smectite, and phyllosilicate. Further, examples of the smectite include bentonite, montmorillonite (MMT), saponite, armargosite, metabentonite, hectorite,  
25 beidellite, stevensite, halloysite, and nontronite.

As the organoclay used in the composition of the

present invention, useful is commercial organoclay sold under the trade name of Cloisite 30B, available from Southern Clay Products, or natural clay, organically modified through various methods known in the art.

5           The coating composition of the present invention may also be used as a solvent-type anticorrosive coating composition, composed mainly of an epoxy resin monomer or oligomer (number average molecular weight of 340~2,000 g/mole), for use in the surface protection of pre-sealed  
10 steel plates and other metals.

A better understanding of the present invention may be obtained through the following examples which are set forth to illustrate, but are not to be construed as the limit of the present invention.

15

#### **Mode for Invention**

##### Example 1

As main components of a solvent-type coating solution, an epoxy monomer having an average molecular  
20 weight of 380 g/mole and a melamine curing agent were used.

Organoclay was dispersed in each of the main components, and in the mixture of the main components, thus preparing nanocomposite type coating compositions.

As the epoxy monomer, YD-128 (diglycidyl ether of  
25 Bisphenol-A, epoxy equivalent weight of 186.4 g/eq, number average molecular weight of 372.8 g/mole), available from

Kukdo Chemical Co. Ltd., was used, and as the curing agent, a melamine derivative, available from Cytec Industries Inc., and DDS (4,4'-diaminodiphenylsulfonate), available from Tokyo Chemical Industry Co. Ltd., were used. The  
5 organoclay Cloisite 30B, available from Southern Clay Products, was used, and this Cloisite 30B was organically modified montmorillonite (MMT) comprising organic material, including a methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium ion, intercalated into the layers thereof.

10 In Table 1 below, the sample 1 was a coating solution having no organoclay, obtained by mixing components using a general stirrer. The sample 2 was obtained by dispersing 2.5 parts by weight of Cloisite 30B to 100 parts by weight of an epoxy monomer for 20 min using ultrasonic waves (max.  
15 power of 750 W), separately dispersing 2.5 parts by weight of Cloisite 30B in 75 parts by weight of a melamine curing agent for 20 min using ultrasonic waves, and mixing the epoxy/organoclay (epoxy monomer having organoclay dispersed therein) and the melamine curing agent/organoclay (melamine  
20 curing agent having organoclay dispersed therein), thus separately prepared, with 10 parts by weight of DDS for 20 min using ultrasonic waves. As the samples 3 and 4, dispersion of 5 parts by weight of organoclay in 100 parts by weight of an epoxy resin and of 5 parts by weight of  
25 organoclay in 75 parts by weight of a melamine curing agent, respectively, was conducted for 20 min using

ultrasonic waves, and then a mixing process was carried out, thus the corresponding coating compositions were obtained. Further, the sample 5 was prepared by mixing, as main components, 100 parts by weight of epoxy, 75 parts by weight of a melamine curing agent, and 10 parts by weight of DDS using a general stirrer and then dispersing 5 parts by weight of organoclay therein for 20 min using ultrasonic waves.

Moreover, the amount of xylene (about 20~40 parts by weight based on 100 parts by weight of epoxy) was controlled and mixed using a general stirrer, so that the five samples of Table 1 had the same viscosity. In this way, because the five samples had the same viscosity, the thickness of coating films obtained through bar coating were the same, and the change in corrosion resistance depending on the composition difference could be estimated.

Each of the five samples of Table 1 was applied on a zinc plated steel plate using bar coater and then allowed to react in an oven, in which the temperature of the steel plate was maintained at 250°C, for 60 sec, leading to a zinc plated steel plate coated with about 2.0 g/m<sup>2</sup> of the coating composition.

Four coated zinc plated steel plates per sample were placed into a saltwater spray tester (SST), and the surface state thereof was photographed at predetermined time intervals. The time that it took for red rust to be

generated was observed with the naked eye and the average value thereof was used to evaluate corrosion resistance. The results are summarized in Table 1 below. As such, the saltwater spray tester was operated at 36°C under conditions of saltwater spray pressure of 1 kg/cm<sup>2</sup> and relative humidity of 99%.

Compared to the sample 1, all coating compositions having 5 parts by weight of the organoclay exhibited improved corrosion resistance.

10

TABLE 1

Results of Corrosion Resistance depending on Composition of Resin, Curing Agent and Organoclay

Sample No.	Resin		Curing Agent			Total Amount of Organoclay based on Epoxy (wt part)	Corrosion Resistance (at 36°C) (hours)
	Epoxy/Organoclay		Melamine Curing Agent/Organoclay		DDS (wt part)		
	Epoxy (wt part)	Organoclay (30B) (wt part)	Melamine Curing Agent (wt part)	Organoclay (30B) (wt part)			
1	100	-	75	-	10	0	264
2	100	2.5	75	2.5	10	5	348
3	100	5.0	75	-	10	5	444
4	100	-	75	5.0	10	5	456
5	100	-	75	-	10	5	348

15

As the results of measurement using an X-ray diffractometer (Pohang Accelerator Laboratory, 4C1 and 5C2, SAXS), the epoxy monomer and the melamine curing agent were penetrated into the galleries of Cloisite 30B in the course of the dispersion, such that the d-spacing of layers increased from 1.8 nm to 8.3 nm and 3.8 nm, respectively.

20

In the case where the dispersion was performed using a general stirrer, no increase in the d-spacing of layers was observed.

5           Example 2

As main components of a solvent-type coating solution, an epoxy monomer having an average molecular weight of 380 g/mole and a melamine curing agent were used. Selectively, as the resin component, polyurethane resin,  
10   having an average molecular weight of 5,000~50,000 and dissolved in xylene, could be further included. Organoclay was dispersed in each of the main components, thus preparing nanocomposite type coating compositions.

In Table 2 below, the sample 7 was prepared by  
15   dispersing 2.5 parts by weight of Cloisite 30B to 100 parts by weight of an epoxy monomer for 20 min using ultrasonic waves (max. power of 750 W), separately dispersing 2.5 parts by weight of Cloisite 30B in 15 parts by weight of a melamine curing agent for 20 min using ultrasonic waves,  
20   and mixing the epoxy/organoclay (epoxy monomer having organoclay dispersed therein) and the separately prepared melamine curing agent/organoclay (melamine curing agent having organoclay dispersed therein) with 10 parts by weight of polyurethane and 10 parts by weight of DDS for 20  
25   min using ultrasonic waves.

The sample 6 was obtained by mixing components, not

using ultrasonic waves but using a general stirrer, due to the absence of organoclay.

As the results of measurement using an X-ray diffractometer (Pohang Accelerator Laboratory, 4C1 and 5C2, SAXS), the epoxy monomer and the melamine curing agent were penetrated into the layers of Cloisite 30B in the course of the dispersion, and thus the d-spacing of layers increased from 1.8 nm to 8.3 nm and 3.8 nm, respectively. In the case where the dispersion was performed using a general stirrer, no increase in the d-spacing of layers was observed.

Further, the amount of xylene was controlled and mixed using a general stirrer, so that the two samples of Table 2 had the same viscosity. Because the two samples had the same viscosity, the thickness of coating films obtained through bar coating were the same, and the change in corrosion resistance depending on the composition difference could be estimated.

Each of the two samples of Table 2 was applied on a zinc plated steel plate using bar coater and then allowed to react in an oven, in which the temperature of the steel plate was maintained at 250°C, for 60 sec, therefore obtaining a zinc plated steel plate coated with about 2.0 g/m<sup>2</sup> of the coating composition.

Three coated zinc plated steel plates per sample were placed into a saltwater spray tester (SST), and the surface state thereof was photographed at predetermined time

intervals. The time that it took for red rust to be generated was observed with the naked eye, and the average value thereof was used to evaluate corrosion resistance. The results are summarized in Table 2 below.

5           As is apparent from the results of saltwater spray test for two coating compositions of Table 2, in the case where no organoclay was added, red rust was generated after 792 hours on average. However, the coating solution having the organoclay had no red rust until 1,848 hours.

10           Also, metal powder for assuring weldability after coating and other additives were added to the anticorrosive coating composition to thus yield a coating solution. Accordingly, the two samples of Table 2 respectively were added with the same amounts of metal powder and the  
15 additives, applied on the zinc plated steel plate, cured, and then tested for corrosion resistance. The resultant corrosion resistance of the coating composition having the organoclay could be confirmed to be superior. Further, the two samples of Table 2 respectively were added with the  
20 same amounts of metal powder and the additives, applied, cured, formed into a cup, and then tested for adhesion. Furthermore, a boiling water adhesion test, in which the formed cup was dipped into boiling water (100°C) for 1 hour and then tested for adhesion, was conducted.

25           For the adhesion test, when adhesive tapes of the same size as each other were attached to the steel plate



and then immediately removed, whether the coating was peeled off or not was observed. Upon the test of adhesion to the cup produced above, the coating did not peel off in either case of the coating solution having no organoclay and the nanocomposite coating solution having organoclay. However, upon the boiling water adhesion test of the produced cup, in the case of the coating solution having organoclay (sample 7), the coating did not peel off, whereas the coating partially peeled off in the case of the coating solution having no organoclay (sample 6). Even upon an adhesion test after cross-cut under conditions more severe than in the production of the cup, in the case of the coating solution having organoclay, the coating did not peel off, and the coating surface was maintained without degrading. For the cross-cut adhesion test, the coating surface was cross-cut into 100 surfaces each having a size of 1 cm x 1 cm using a blade, after which adhesive tape was attached thereto and then removed to thus evaluate the adhesion.

20

25

TABLE 2

Results of Corrosion Resistance depending on Composition of  
Resin, Curing Agent and Organoclay

Sample No.	Resin			Curing Agent			Total Amount of Organoclay based on Epoxy (wt part)	Corrosion Resistance (at 36°C) (hours)
	Epoxy/Organoclay		Poly-urethane (wt part)	Melamine Curing Agent/Organoclay		DDS (wt part)		
	Epoxy (wt part)	Organoclay (30B) (wt part)		Melamine Curing Agent (wt part)	Organoclay (30B) (wt part)			
6	100	-	10	15	-	10	0	792
7	100	2.5	10	15	2.5	10	5	at least 1,848

5

Example 3

In the same manner as in Example 1, organoclay (Cloisite 30B) was dispersed in an epoxy oligomer having an average molecular weight of 2,000 g/mole using a sonicator (max. power 750 W) and then mixed with other components using a sonicator, thus preparing a coating composition (sample 9). The components and weight ratios thereof are summarized in Table 3 below.

Further, in the same manner as in Example 1, the coating composition was applied on a zinc plated steel plate and then cured in an oven. Three coated zinc plated steel plates per sample were placed into a saltwater spray tester (SST) to thus measure corrosion resistance. Unlike Examples 1 and 2, in Example 3, the SST was operated at 42°C, so that red rust was quickly generated. The time periods required for generating red rust on the surface of the coated zinc plated steel plate were averaged. The

results are shown in Table 3 below.

The corrosion resistance of the coating composition having organoclay (sample 9) was 744 hours on average, and was thus superior to that of the coating composition having  
5 no organoclay (sample 8).

TABLE 3

Results of Corrosion Resistance depending on Composition of Resin, Curing Agent and Organoclay

10

Sample No.	Resin			Melamine Curing Agent (wt part)	Total Amount of Organoclay based on Epoxy (wt part)	Corrosion Resistance (at 42°C) (hours)
	Epoxy (wt part)	Organoclay (30B) (wt part)	Polyurethane (wt part)			
8	100	-	10	15	0	456
9	100	5	10	15	5	744

#### Example 4

Compared to Examples 1 and 2, in which the organoclay was used in an amount of 5 parts by weight based on 100 parts by weight of the epoxy monomer to thus prepare the  
15 coating composition having organoclay, the coating composition was prepared using the organoclay in different amounts so as to determine the optimal amount of the organoclay. Further, unlike Examples 1,2 and 3 dispersion  
20 and mixing using ultrasonic waves were conducted only once. That is, when the samples 11, 12 and 13 of Table 4 were prepared, an epoxy monomer, polyurethane, a melamine curing agent, DDS and organoclay were mixed together as shown in

Table 4 below, and then dispersed for 20 min using ultrasonic waves. In the sample having no organoclay, red rust was observed after 288 hours, whereas the sample having organoclay had no red rust even after 288 hours.

5 When the amount of the organoclay was 2.5 parts by weight, red rust was observed after 624 hours, which was above 100% higher than in the coating composition having no organoclay. Furthermore, the use of the organoclay in an amount of 6.5 parts by weight resulted in the generation of

10 red rust after 720 hours, and the use of the organoclay in an amount of 4.5 parts by weight resulted in the generation of red rust after 792 hours. Thereby, the optimal amount of the organoclay, which was added to the organoclay-containing coating solution for application on a steel

15 plate, was determined to be about 4.5 parts by weight.

The coating solution containing 4.5 parts by weight of the organoclay was applied on a steel plate and then cured, after which a coating layer was separated in the form of a film and thus analyzed using an XRD (Pohang

20 Accelerator Laboratory, 5C2, SAXS). Although the intrinsic d-spacing of Cloisite 30B was 1.8 nm, the d-spacing after curing was measured to be 4.7 nm. From this, it could be confirmed that the clay was efficiently dispersed. Thanks to the efficient dispersion of the organoclay, the barrier

25 property was improved, leading to superior corrosion resistance.

TABLE 4  
Results of Corrosion Resistance depending on Amount of  
Organoclay

Sample No.	Epoxy (wt part)	Poly-urethane (wt part)	Melamine Curing Agent (wt part)	DDS (wt part)	Organoclay (wt part)	Corrosion Resistance (at 42°C) (hours)
10	100	10	15	10	0	288
11	100	10	15	10	2.5	624
12	100	10	15	10	4.5	792
13	100	10	15	10	6.5	720

5

#### Example 5

The components of a coating composition for application on a zinc plated steel plate, other than the organoclay, were not changed, but the dispersion process was varied when the organoclay was added in an amount of 3 parts by weight or 5 parts by weight based on the amount of resin, thus preparing samples. In the samples 14, 15, and 16 of Table 5, the sample 14 had no organoclay, and the sample 15 was prepared in such a manner that both dispersion of the organoclay in epoxy and a melamine curing agent and mixing into a coating composition were conducted using a general stirrer for 20 min. Further, the sample 16 had the same composition ratio as in the sample 15, with the exception that both dispersion of the organoclay in epoxy and a melamine curing agent and mixing into a coating composition were performed using a sonicator for 20 min. The coating process and the curing process were applied as above, and the corrosion resistance was measured using an

SST at 42°C.

As is apparent from the results of the test of corrosion resistance, the organoclay could be seen to contribute to increased corrosion resistance. Further, when  
5 the organoclay was dispersed and mixed using a sonicator, the resin or curing agent was diffused into the galleries of the organoclay, thus realizing superior corrosion resistance to that of the coating composition prepared through simple mixing using a general stirrer. In the  
10 samples 17, 18, 19, and 20 of Table 5, which had the same composition ratio, the sample 17 was prepared by dispersing the organoclay using a general stirrer, and the samples 18, 19 and 20 were prepared in such a manner that the organoclay was dispersed in epoxy, the melamine curing  
15 agent, and epoxy/melamine curing agent, respectively, using ultrasonic waves, and then a mixing process was performed using a sonicator.

In the case where the dispersion of the organoclay in the epoxy or the melamine curing agent and the mixing  
20 thereof were conducted using ultrasonic waves (samples 18, 19, 20), corrosion resistance was 408~444 hours, which was superior compared to when no ultrasonic waves was used (sample 17).

25

TABLE 5

Sample No.	Epoxy/Organo clay		Melamine Curing Agent/Organoclay		Organo clay (wt part)	DDS (wt part)	Total Amount of Organo clay (wt part)	Method of Dispersing	Corrosion Resistance (at 42°C) (hours)
	Epoxy (wt part)	Organo clay (wt part)	Melamine Curing Agent (wt part)	Organo clay (wt part)					
14	100	-	15	-	-	-	0	General Stirrer	120
15	100	2.5	15	2.5	-	-	5	General Stirrer	240
16	100	2.5	15	2.5	-	-	5	Ultrasonic Waves	408
17	100	-	15	-	3	10	3	General Stirrer	228
18	100	3	15	-	-	10	3	Ultrasonic Waves	408
19	100	-	15	3	-	10	3	Ultrasonic Waves	444
20	100	1.5	15	1.5	-	10	3	Ultrasonic Waves	444

## 5 Industrial Applicability

As described above, organoclay is dispersed in each of the main components of a coating composition or in a mixture of the main components using ultrasonic waves, after which these components are mixed with an additive, thus preparing a coating composition. The coating composition thus prepared has corrosion resistance superior to that of conventional coating compositions containing

organoclay, and furthermore, has good properties, including weldability and adhesion. Accordingly, the coating composition of the present invention can be efficiently applied not only on a zinc plated steel plate but also on  
5 other metals, thereby remarkably increasing corrosion resistance.



**CLAIMS**

1. An anticorrosive coating composition, comprising  
100 parts by weight of an epoxy resin monomer or oligomer,  
5~80 parts by weight of a curing agent having two or more  
5 amine functional groups, and 0.1~20 parts by weight of  
organoclay, which is uniformly mixed and dispersed in  
either or both of the epoxy monomer or oligomer and the  
curing agent.
2. The composition according to claim 1, wherein the  
10 organoclay is mixed and dispersed using ultrasonic waves.
3. The composition according to claim 1, wherein the  
epoxy monomer or oligomer has a number average molecular  
weight of 340~2,000 g/mole.
- 15 4. The composition according to claim 1, wherein the  
organoclay is selected from the group consisting of  
smectite clays having a layered structure, including  
montmorillonite, hectorite, halloysite, bentonite,  
nontronite, and beidellite, each of which is natural or  
20 synthetic.
5. The composition according to claim 4, wherein the  
organoclay is organically modified montmorillonite,

comprising a methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium ion, intercalated into layers thereof.

6. The composition according to claim 1, wherein the  
5 organoclay is contained in an amount of 3~6 wt% based on an amount of the epoxy monomer.

7. The composition according to claim 1, further  
comprising an additive selected from the group consisting  
10 of alumina sol, silica sol, metal powder, wax, and a phosphate-based rust inhibitor.

8. The composition according to claim 1, wherein the  
epoxy monomer is a modified epoxy monomer containing a  
15 halogen group or an amine group.

9. A method of preparing a uniformly dispersed organoclay-containing anticorrosive coating composition, comprising:

20 (i) uniformly dispersing 0.1~20 parts by weight of organoclay in either or both of 100 parts by weight of an epoxy resin monomer or oligomer and 5~30 parts by weight of a curing agent having two or more amine functional groups using ultrasonic waves, and then mixing the epoxy resin  
25 monomer or oligomer and the curing agent, either or both of which have the organoclay dispersed therein, or

(ii) mixing 100 parts by weight of an epoxy resin monomer or oligomer and 5~30 parts by weight of a curing agent having two or more amine functional groups, and then uniformly dispersing 0.1~20 parts by weight of organoclay  
5 therein using ultrasonic waves.

10. The method according to claim 9, further comprising adding and mixing an additive, selected from the group consisting of alumina sol, silica sol, metal powder, wax, and a phosphate-based rust inhibitor, to the mixture  
10 of the epoxy resin monomer or oligomer and the curing agent, in which the organoclay is dispersed, after (i) or (ii).

15 11. A zinc plated steel plate, coated with the anticorrosive coating composition of claim 1.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/KR2006/004588**A. CLASSIFICATION OF SUBJECT MATTER***C23C 22/00(2006.01)i*

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC8 C08L 63/00, C09K 3/14, C09D 5/02, C09D 7/12, C09D 201/00, C23C 22/12, C23C 22/46, C23C 22/56, C23C 26/00, C23C 28/00.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Patents and applications for inventions since 1975.

Korean Utility models and applications for Utility models since 1975.

Japanese Utility models and applications for Utility models since 1975.

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS(KIPO internal) &amp; keywords: anticorrosion, polymer, clay, nanocomposite and similar terms.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	KR 10-2005-0063979 A (POSCO & POSTECH FOUNDATION) 29 June 2005 See the abstract, examples 1-3, and claims 1-4. (cited in the applications)	1, 2, 6 - 11 3 - 5
A	US 6569214 B2 (U.S. TECHNOLOGY CORPORATION) 27 May 2003 See the abstract and claims 1-10.	1 - 11
A	JP 2002-030255 A (NIPPON PARKERIZING CO. LTD.) 31 January 2002 See claims 1-5.	1 - 11
A	JP 2004-197113 A (NIPPON STEEL CORP.) 15 July 2004 See claims 1-7.	1 - 11



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

01 FEBRUARY 2007 (01.02.2007)

Date of mailing of the international search report

**01 FEBRUARY 2007 (01.02.2007)**

Name and mailing address of the ISA/KR

Korean Intellectual Property Office  
920 Dunsan-dong, Seo-gu, Daejeon 302-701,  
Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

LEE, SUNG JOON

Telephone No. 82-42-481-5530



**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

PCT/KR2006/004588

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 10-2005-0063979 A	29.06.2005	NONE	
US 6569214 B2	27.05.2003	AU200185032A1	15.05.2002
		US2002011030AA	31.01.2002
		US2003181548A1	25.09.2003
		US2006142435AA	29.06.2006
		US7037969BB	02.05.2006
		W00236307A1	10.05.2002
JP 2002-030255 A	31.01.2002	NONE	
JP 2001-197113 A	15.07.2001	NONE	